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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Improvements in or relating to Methods of Controlling the Spacial Distribution of an Evaporated Film of Getter Material within the Evacuated Vessel or Tube of an Electron Discharge Device

We, S.A.E.S. GETTERS S.p.A., an Italian Company, of Via Gallarate, 215, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methods of controlling the spacial distribution of an evaporated film of getter material within the evacuated vessel or tube of an electron discharge device such as a cathode ray tube.

It is well known that, in order to maintain the required degree of vacuum in, for example, television picture tubes, as well as in many other types of electron tubes, the generally used technique is to employ an internal chemical pump or getter. The getter consists of a thin metallic film deposited on appropriate surfaces of the device after it has been processed and isolated from the conventional pumps. This thin metallic film is usually barium and is commonly deposited from a getter container which may be heated by externally induced radio frequency currents. The getter container consists of a non-magnetic stainless steel ring of U shaped section in which is usually compressed in equal proportions a mixture of powdered 50% barium — 50% aluminium alloy and nickel. On heating, as previously mentioned by externally induced radio frequency currents, an exothermic reaction occurs between the barium-aluminium alloy and the nickel when the temperature is about 800°C causing an instantaneous and spontaneous increase in temperature up to above 1300°C with the consequent evaporation of 30 to 40% of the barium within the container. Since, however, the radio frequency power is still applied to the getter container the remaining barium also evaporates but at a much decreased rate. Another type of getter is also known where no such reaction occurs due to the absence of the nickel and as a consequence this type of getter is called endothermic. Its main disadvantage is the irreproducibility of yield and as a consequence it is rarely employed in manufacturing processes. The barium film obtained from either of these two processes is very active chemically, it reacts with the residual gases present in the tube and efficiently removes them from the gaseous phase. Furthermore, the action of the barium film is not instantaneous or short lived, but by means of diffusion phenomena it is capable of continuing its gettering or pumping action throughout the life of the tube.

It is well known that the rate of reaction of the residual gases in the tube with the barium film increases proportionally with the latter's increase in surface area. It is for this reason that in electron tubes, and in particular in television picture tubes, the greatest possible internal surface area is utilized for film deposition. This naturally results in the complete coverage of the screen of the television tube with barium. In fact due to the position of the getter container, which is mounted on the top of the electron gun which is in turn situated on the normal to the centre of the screen, and as a result of the well known distribution laws of evaporation, a substantial fraction of the barium evaporated is deposited on the screen of the television picture tube. Its distribution is circularly symmetrical and is a maximum at the centre of the screen and a minimum on its periphery.

The image on the screen of a television picture tube is due to the high energy electrons which impinge and excite suitable phosphors evenly distributed on the internal surface of the screen. To increase the luminescence of these phosphors in the forward

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direction it is standard practice to cover them, on the side from which the electrons are incident on them, by a thin layer of aluminium which has also other electrical functions connected with the potential distribution within the tube the protection of the phosphors from ion burn, etc. The presence of this aluminium film causes a loss in energy of the electrons which are directed at the phosphors and so decrease their luminosity. The same effect is also caused by the barium present on the screen and although its thickness is much less than that of the aluminium its effects are more pronounced due to its higher molecular mass. As previously mentioned the thickness of the barium film is greatest at the centre of the screen and it is here that electrons are decelerated to a greater extent. This sometimes causes the characteristic darker central portion in the image on the screen and can only be avoided by using higher electron accelerating potentials in the design of the set with consequent increase in production costs.

The advantages which would result in television tube production and usage, and in similar electron devices, if the barium film on the screen could be rendered more uniform and thinner are obvious. In fact if such a solution were possible a very appreciable economic saving would result in the production of television sets and similar devices. If such a saving were not required advantage could be taken from the reduced barium film thickness to improve the quality of the tube. Some cases exist where tubes are produced without aluminium backing of the phosphors and in these cases no barium must be deposited on the phosphors since they would be damaged.

Hence in all the above mentioned cases the use of a suitable device and technique for efficiently controlling the barium deposition on the screen of the tube would be extremely useful for the industry as a whole.

The methods employed heretofore for controlling the barium film thickness on the screen of television picture tubes, and similar electron devices, have relied principally in mechanically directing the issuing barium vapour by means of various types of deflecting baffles fashioned on the getter container. In one particular embodiment of this procedure the baffles are such as to direct the barium vapours towards the centre of the bulb, i.e. on the normal to the centre of the screen of the tube. The coverage being so adjusted as to cause collisions between the barium atoms before they reach the screen and thus cause a virtual point source of barium atoms from which they may evaporate in all directions. In still another embodiment using mechanical direction of the barium vapours the container of the getter has baffles which direct the evaporating barium atoms in a direction perpendicular to that of the normal to the centre of the screen. Various other solutions between these two extremes have also been suggested and adopted. However, their major drawback has been their low efficiency or if efficient the fact that they limit to a very great extent the surface area of the film which they produce and thus render it ineffective for the purposes required. The only virtue of some of these methods of mechanically directing the barium evaporation, however, inefficiently, has been to reduce the quantity of barium reflected towards the electron gun. In fact barium evaporated in this direction can be extremely troublesome since it can give rise to secondary emission effects, short circuits, etc.

Thus, the principal object of the present invention is to provide a means of reducing the quantity of barium or other getter, reaching the screen of a television picture tube or similar device, if required even to zero, and to redistribute the excess barium on other internal surfaces which have up till now been less utilised, for example the cone area.

According to the present invention a method of controlling the spacial distribution of an evaporated film of getter material within the evacuated vessel or tube of an electron discharge device, such as a cathode ray tube, comprises the step of introducing into the vessel or tube a gas which is capable of being sorbed by the getter and, at the commencement of the evaporation of the getter material, is at a pressure which serves to provide the said control of spacial distribution.

The gas properties and conditions of pressure should be such that the mean free path of the evaporated getter metal atoms is comparable or less than the distance between the evaporation source and a relevant portion of the vessel or tube, such as the screen of a cathode ray tube, whereby the spacial distribution of getter thereon can be controlled or prevented.

Thus, in the case of a cathode ray tube, the evaporation of the getter occurs in the presence of a suitable gas having an adequate molecular mass and present at a predetermined pressure so that the mean free path of the barium or other atoms in it is smaller than the distance between getter container and screen. With advantage the said gas is completely sorbed by the film of getter material, the said sorption consuming only a fractional portion of the gettering capacity of the film. This sorption should take place in a very short time and, in many cases, the last of the barium, or other get-

ter, to leave the getter container does not find in its way any gas and, not being hindered, can be deposited according to the known distribution laws. However, if no barium is required on the screen the heating of the getter container can be stopped immediately after having initiated the exothermic reaction. The most suitable gas to employ is nitrogen, the working pressure being between 5 x 10^{-2} and 1 x 10^{-3} torr. The nitrogen may be introduced into the tube in the form of a stable compound, which will dissociate only at temperatures immediately below the onset of the exothermic reaction so that the gas is present in the tube before the onset of such exothermic reaction.

Processes are already known whereby continuous evaporation of materials in an inert gas atmosphere is utilized for the production of powders characterized by very fine particle size. However, it must be realized that in television picture tubes and similar electron devices such fine particles must be avoided at all costs and that, therefore conditions leading to such phenomena must be avoided.

An advantage of the present invention rests in the fact that a suitable choice of gas and pressure enables the control of up to 50% of the barium which may be obtained from an exothermic type getter without producing any fine particles and without leaving a high pressure in the tube at the end of the evaporation process. Thus this fraction of the barium is deposited only in the cone and neck zones of the television picture tube, whilst the rest of the barium is evenly distributed on these and the remaining internal surface areas of the tube. Should no barium be required on the screen this result can also be obtained by interrupting the heating of the getter container once having initiated the exothermic reaction.

In addition to rendering possible a fine control of the distribution of the barium film, the use of getters according to the concepts of the present invention produces barium films, as already known in the art, characterized by a high porosity and so increases appreciably the real surface of the film produced. Practical tests have shown that this increase in specific surface area involves an increase of sorption characteristics by a factor of 2 to 3. This fact presents obvious advantages from the point of view of tube life or from an economic stand point. Such porous films are a result of submicroscopic globule formation in the vapour phase which condense as such on the walls of the vessel.

To put the inventive process into practice any gas may at first sight appear suitable. However, the following points should be borne in mind when trying to decide on the nature of the gas to be employed. Its retarding and deflecting action increases with:

a) increase in molecular mass,
b) increase in pressure,
c) decrease in chemical affinity to barium.

Another point to observe as far as regards b) is that the pressure used should not be too high since it could cause a serious decrease in gettering capacity of the getter film.

On the basis of the above considerations the rare gases, such as argon, krypton, etc. would seem very attractive. However, these gases are not sorbed by the getter material and so if the getter film is deposited, as occurs usually, in the closed tube the rare gases would remain in it rendering its function impossible. Therefore such gases may not be utilized for the purposes of the present invention. Other gases such as hydrogen, carbon monoxide, carbon dioxide and oxygen may be considered. However, such gases would produce results extremely detrimental to tube characteristics as such and they tend to produce hydrocarbons, water vapour, etc. which are harmful to cathode activity. Further, the use of all these gases would be contrary to one or more of the three points previously indicated. In fact for hydrogen a high pressure would be necessary due to its particularly low mass. For the other three gases a high pressure would be necessary to cope with the extremely high reaction rates which they present with pure barium films.

The gas found to be the most suitable for achieving the objects of the present invention is nitrogen. In fact this gas does not damage the cathode, does not produce undesirable side products, it has a relatively high mass, it is not exceedingly reactive with barium, although it is easily sorbed by it, and as a consequence the pressure necessary to obtain the desired effect is rather low. The nitrogen pressure which has proved to be most satisfactory for the purpose of the present invention is of the order of between 5 x 10^{-2} and 1 x 10^{-3} torr. Pressures above 5 x 10^{-2} torr use up too great a fraction of the barium film and pressures below 10^{-3} torr are not suitable for carrying out the present invention.

The introduction of the selected gas into the tube may be carried out in a number of ways. One of these could be to introduce the required pressure in the tube whilst still on the pump and just before sealing off. However, such a method would not be technically economical. Hence, we propose to introduce the gas into the tube by utilising a compound of nitrogen which will be dissociated by heating prior to evaporation

of the barium. Such a compound could be in powdered form and be mixed in the correct proportions with the getter alloy in the container, it could also be mounted on a separate support removed from the getter, and it may even be that the actual getter container has been subjected to a nitrogenating action giving rise to suitable compounds. However, the compound employed must be stable to all possible ageing and pretreatments such as deionized water wash, drying and vacuum heat treatments up to 400°C. The compound used should, if mounted in the getter container, dissociate at temperatures below that at which the exothermic reaction sets in. The use of barium azide for example has been long known. However, barium azide would not be usable since its extreme instability to ageing under normal atmosphere conditions or to heating under vacuum are well known.

Non limiting examples of compounds suitable for use in carrying out the present invention are those obtained from nitrogen and any of the following metals or alloys thereof: nickel, iron, molybdenum, manganese, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, tungsten, cobalt, silicon and stainless steel.

As previously mentioned the nitrogen bearing compound may be mixed with the exothermic charge in the getter container, it may be physically separated from it and thus the gas it contains may be evolved a priori before heating the getter container or the getter container itself may be nitrogenated. The concept of the invention, although essentially for exothermic getters, cannot be excluded from use in endothermic getters. However, since in this case the evaporation is initially low and then picks up speed the quantity of gas must be initially low and must slowly increase as the rate of evaporation rises. In the case of exothermic getters since, as previously mentioned, 30 to 40% of the barium is emitted spontaneously, the nitrogen pressure present has full effect on this quantity of barium. The remaining barium which evaporates at a slower rate is less influenced due to the sorption of nitrogen which has taken place. Nevertheless an appreciable influence is also exercised on this second quantity of barium.

The exothermic getter, containing the nitrogenous compound most suitable, and having any desired or suitable deflecting baffles arrangement can be mounted as the normal and more conventional getter on the electron gun of the tube or in any required or desired position. The usefulness of the baffles is, however, very limited with getters used in carrying out the present invention as far as concerns the barium film distribution on the screen and on the cone of the television picture tube. Baffles are however still useful for controlling back evaporation of barium towards the gun of the tube.

A method of carrying out the invention will now be described in greater detail by way of example with reference to the accompanying drawings in which:—

Figure 1 shows diagrammatically a cathode ray tube accompanied by explanatory curves; and

Figures 2 and 3 are further explanatory curves.

Referring to Figure 1 of the drawings, the television picture cathode ray tube shown has a flare angle of 110° and is provided with a conventional getter G mounted 1 1/16" from the yoke reference line (Y.R.L.) and consisting of a powdered mixture of equal proportion of 50% Ba-50% aluminium alloy and nickel supported in a stainless steel container of ring shape. The getter is evaporated under good vacuum conditions producing the distribution of barium in the tube indicated by the diagrams (a) and (b) in Figure 1 which refer to the barium thickness on the screen and the cone sections of the tube respectively. The dashed lines, 1 and 3, indicate the distribution of the above mentioned type of getter. It will be noted that the thickness of the film at the centre of the screen is 1400 Ångström units. In a similar tube was then mounted a getter of exactly similar characteristics as above but containing also a predetermined quantity of powdered iron nitride (Fe_4N) such as to produce in the tube a pressure of about 1 x 10[illegible] torr of nitrogen during the normal flashing of the getter and prior to the onset of the barium evaporation due to the exothermic reaction. In this case the barium film distribution in the tube was that shown by the continuous lines 2 and 4. It will be noted that the thickness of the barium film at the centre of the screen is less than 400 Angström units in this case.

The relative quantities of barium on the screen, cone and neck of the tube with conventional getters are respectively 7.0, 1.8, 16.2 mg and with the getters according to the present invention they are respectively 2.5, 3.5, 19.0 mg. Such significant reduction of barium on the screen is very useful for electron transparence and results in an increased light output from the tube of up to 30%.

The fact that evaporation of the barium film in a nitrogen atmosphere in no way reduces characteristics of the barium film produced is illustrated in Figure 2. In this Figure the gettering rates V (cm^3 sec^{-1}) of carbon monoxide are plotted against the related quantities Qt (cm^3 torr) of carbon monoxide sorbed. The television picture tube and getter types as well as position are assumed to be the same as those previously

mentioned. The gettering characteristics were, also in this case, measured for a 25 mg Ba film and the constant CO pressure on the getter was 5.10^{-6} torr. Curve 5 refers to the characteristics of a conventional getter film whilst curve 6 refers to those of a film obtained according to the present invention. It will be observed that the gettering characteristics of the film obtained by evaporating the barium film in a nitrogen pressure have increased since the amount of barium rendered accessible to the gas has been increased appreciably due to the increase in specific surface area of a film formed in this manner.

The curves in Figure 3 clearly show the retarding action of the gas introduced on the forward evaporation of barium and were obtained by using a quartz crystal film thickness monitor. The crystal was mounted in a tube similar to that described and at the centre of the screen. The shift of frequency of the crystal as barium is deposited on one of its faces is a direct measure of the quantity of barium condensed on the face itself. In Figure 3 the percentages of barium thickness with reference to a conventional getter at the end of evaporation are plotted against the time of evaporation. The external radio frequency power is applied at zero time (not shown). The starting times indicated at S_1 and S_2 show the instant when the exothermic reaction begins, whilst the total times T_1 and T_2 are the times at which the radio frequency current to the getter container is discontinued. The curve 7 refers to the conventional getter, whilst curve 8 refers to a getter according to the present invention. It will be clearly observed how the gas present in the getter, and liberated in the tube before the starting time, has its principle action essentially during the first few seconds of evaporation although even in the subsequent stages a certain action is also being exercised. It should however be noted that all the gas introduced after a few minutes has been repumped or taken up by the getter as has been revealed by pressure measurements carried out during these tests.

WHAT WE CLAIM IS:—

1. A method of controlling the spacial distribution of an evaporated film of getter material within the evacuated vessel or tube of an electron discharge device, such as a cathode ray tube, comprising the step of introducing into the vessel or tube a gas which is capable of being sorbed by the getter and, at the commencement of the evaporation of the getter material is at a pressure which serves to provide the said control of spacial distribution.

2. A method as claimed in claim 1 in which the gas properties and conditions of pressure are such that the mean free path of the evaporated getter metal atoms is comparable or less than the distance between the evaporation source and a relevant portion of the vessel or tube, such as the screen of a cathode ray tube, whereby the spacial distribution of getter thereon can be controlled or prevented.

3. A method as claimed in either of claims 1 or 2 in which the gas is nitrogen and the working pressure is between 5 x 10^{-2} and 1 x 10^{-3} torr.

4. A method as claimed in any one of claims 1 to 3 in which a compound, which is not appreciably dissociated during any preliminary treatment of the vessel or tube or during exposure to air, is introduced to the vessel or tube together with the getter material and admixed therewith or mechanically separated therefrom, the compound being capable of evolving the said gas upon heating.

5. A method as claimed in claim 4 in which a compound is used which is dissociated at temperatures lower than those at which evaporation of getter metal atoms commences.

6. A method according to claim 4 or 5 in which a compound is used which is dissociated at temperatures lower than those at which evaporation of getter metal atoms begins and which continues to emit gas throughout the process of evaporation.

7. A method according to any of claims 4, 5 or 6 in which nitrogen is introduced in the vessel or tube in the form of metallic nitrogen compound.

8. A method according to claims 4, 5 or 6 in which nitrogen is introduced in the vessel or tube in the form of nitrogen contained as a chemical compound in the support for the getter metal to be evaporated.

9. A method according to any of the preceding claims, in which the getter material is introduced into the vessel or tube on a supporting member fitted with baffles which limit the distribution of the getter towards an electron gun of the said vessel or tube.

10. A method according to any one of claims 1-9 in which the said gas is completely sorbed by the film of getter material the said sorption consuming only a fractional portion of the gettering capacity of the film.

11. A getter material with which is mixed a nitrogen bearing compound which, although stable to air and to heat treatments up to 500°C, dissociates liberating nitrogen when heated within an electron discharge device.

12. A getter material as claimed in claim 11 which is of the type in which an exothermic reaction is set up on heating, and in which the nitrogen bearing com-

pound dissociates liberating nitrogen when heated within an electron discharge device before the getter begins to evaporate at 800-900°C.

13. An electron tube, vessel or the like, particularly a television picture cathode ray tube, having on its inner face a getter film uniformly distributed thereover and produced by a method according to any of claims 1 to 10.

14. A method of controlling the spacial distribution of an evaporated film of getter material within the evacuated vessel or tube of an electron discharge device, such as a cathode ray tube, substantially as hereinbefore described.

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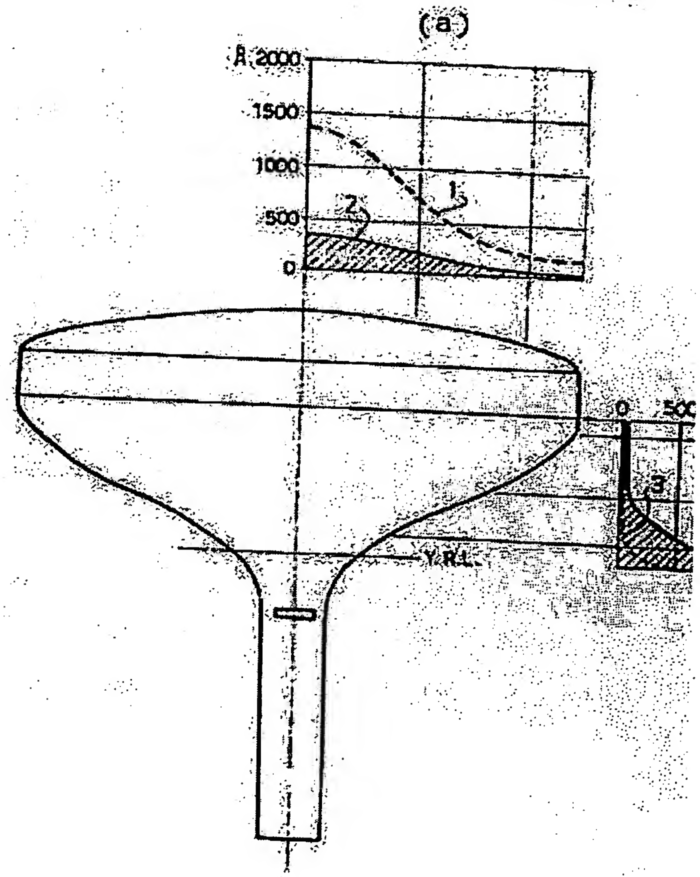
Fig.1



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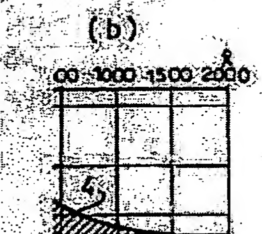


Fig.2

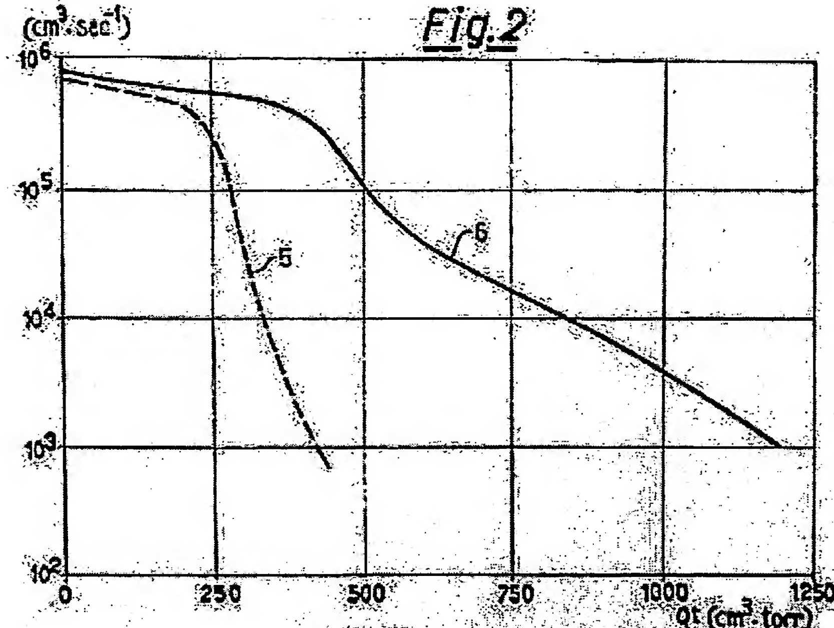
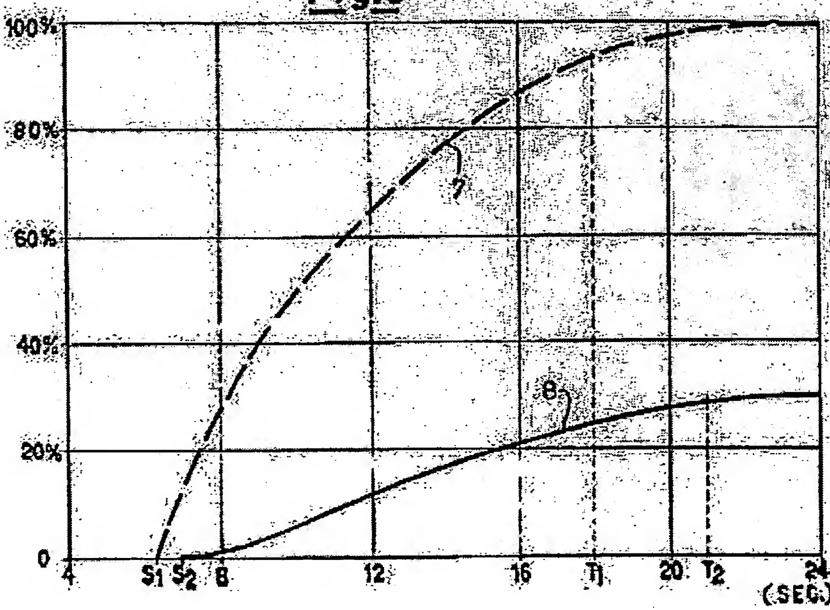


Fig.3



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SHEETS 1 & 2

Fig.1

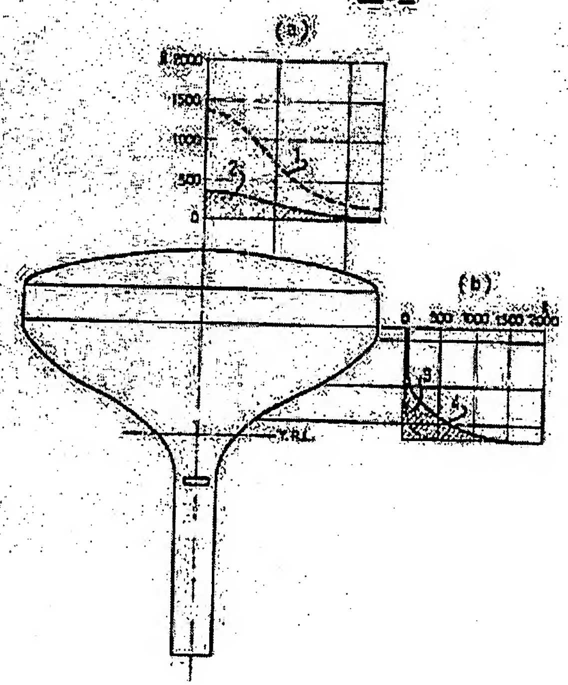

Fig.2

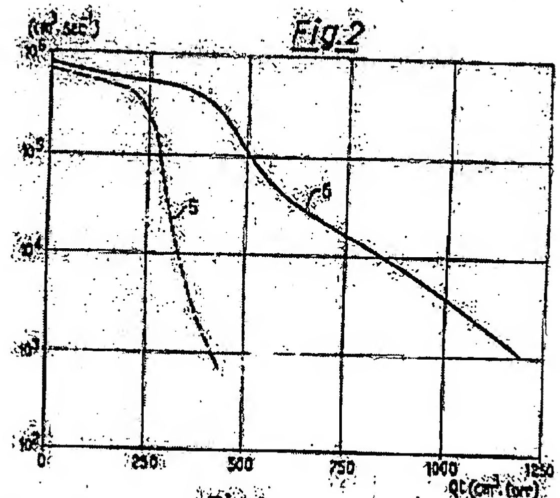

Fig.3